ADSORPTION BY ORGANO-CLAY COMPLEXES

by

C. T. COWAN[1] AND D. WHITE

Gas Research Dept., The University, Leeds 2

ABSTRACT

The adsorption of phenols from dilute aqueous solution by *n*-aliphatic amine and Ethomeen clays has been investigated and it is shown that dodecylammonium bentonite is the most active member of the series ethylammonium to octadecylammonium bentonite. On the basis of spatial considerations, thermodynamic data, and electron density measurements a theory of adsorption has been proposed in which it is envisaged that condensation of adsorbate molecules on the organo-clay surface occurs through electrostatic/hydrogen bond forces at the hydrophilic sites and van der Waals forces at the organophilic sites.

INTRODUCTION

It has been shown that the clay mineral montmorillonite adsorbs many organic compounds such as alcohols (MacEwan, 1948), dihydric alcohols (Mackenzie, 1948), glycols (Bradley, 1945) and nitriles (Brown, reported in MacEwan, 1951, p. 114) but when the clay is immersed in a dilute aqueous solution of these compounds preferential adsorption of the solvent occurs.

Jordan (1949) has shown that by replacing the exchangeable inorganic cations of montmorillonite with large organic amine ions, the low temperature endothermic DTA peak, associated with hygroscopic moisture and cation hydration water, decreased with increasing amine size and from this he concluded that the hydrophilic properties of the clay were decreased. By extending this reasoning to the problem under investigation, it was considered that the amine clay derivatives may, when immersed in a dilute aqueous solution of phenols, show preferential adsorption of the organic material.

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[1] Present address: The Fullers' Earth Union Ltd., Redhill, Surrey.

EXPERIMENTAL

A series of amine and Ethomeen[1] derivatives of purified montmorillonite (Cowan and White, 1958) were prepared by the normal exchange technique, washed by filtration, dried at 65 °C and ground to pass a 200-mesh B.S.S. sieve. These materials were used as adsorbents for various phenols from dilute aqueous solutions as detailed in Table 1.

TABLE 1.– DETAILS OF THE SYSTEMS INVESTIGATED IN THE ADSORPTION
EXPERIMENTS

Adsorbent		Adsorbate	Temperature (°C)
Amine Ions Initially Sorbed on Clay	Amine concentration (meq/100 g clay)		
C_2, C_4, C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18} n-primary aliphatic	70–140	Phenol	20
Dodecylamine	70–140	Phenol	20, 40, 60
C/12, C/15, C/20, C/25 S/12, S/15, S/20, S/25, S/60 T/12, T/15, T/25 18/12, 18/15, 18/20, 18/60 Ethomeens	118	Phenol	20
Dodecylamine	118	Phenol o, m, p-Cresol Pyrocatechol Resorcinol Hydroquinone	20

RESULTS AND DISCUSSION

Using the Freundlich isotherm (which was found by statistical methods to be applicable) and normal thermodynamic equations, the results given in Figs. 1 and 2 and Table 2 were obtained.

The main factors that effect adsorption may be enumerated as follows: (a) The nature of the sites available for condensation of the adsorbate molecules; (b) the nature of the adsorbate molecules; (c) spatial considerations; (d) thermodynamic quantities; and (e) solubility of the adsorbate in the solvent.

In Fig. 2 it is noted that maximum phenol adsorption occurs (under standard conditions) with dodecylammonium bentonite, and increase or decrease in the size of the substituting ion reduces adsorption. Further

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[1] Tertiary amines of the general formula $C_n H_{2n+1} N \Big\langle {(CH_2\ CH_2\ O)_x\ H \atop (CH_2\ CH_2\ O)_y\ H}$, and supplied by Armour and Company Ltd.
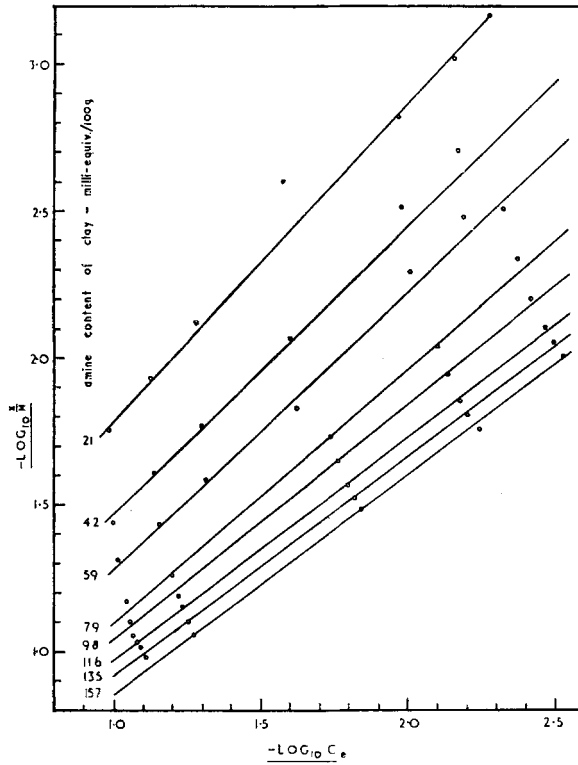
FIGURE 1. — Freundlich isotherms for the adsorption of phenol by various dodecyl-ammonium bentonites at 20 °C.

TABLE 2. — ADSORPTION DATA FOR THE SYSTEMS AMINE CLAY–
PHENOL–WATER

	$\log_{10} C_e$	$-\log_{10} \dfrac{x}{m}$		
	1.0	1.5	2.0	2.5
Ethylamine	1.8885	—	—	—
Butylamine	1.765	—	—	—
Hexylamine	1.695	—	—	—
Octylamine	1.100	1.535	2.000	2.480
Decylamine	1.035	1.455	1.875	2.310
Dodecylamine	0.930	1.330	1.720	2.130
Tetradecylamine	0.970	1.385	1.835	2.365
Hexadecylamine	1.030	1.580	2.130	2.685
Octadecylamine	1.125	1.710	2.290	2.890

understanding of these data can be obtained by considering the results in the light of the adsorption criteria.
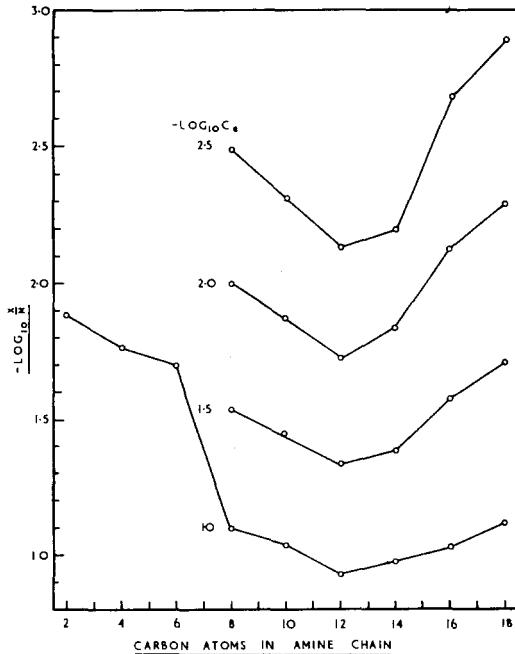

FIGURE 2.—The adsorption of phenol by amine clays as a function of amine chain length (all clays contain 118 meq of amine per 100 g of clay).

The Nature of the Adsorption Sites

Condensation of the phenol molecules on the interlamellar surface may occur because of nonpolar attractive forces such as van der Waals bonding between the phenyl portion of the adsorbate molecule and the alkyl chain of the amine ion, or alternatively by electrostatic/hydrogen bonding between the polar hydroxyl group of the phenol molecules and the exposed hydrophylic clay surface. Increase in the size of the substituting amine ion will increase the magnitude of the nonpolar attractive forces and hence increase adsorption. On the other hand such an increase in amine size will be accompanied by a decrease in the amount of natural clay surface and hence will reduce the magnitude of the polar bond forces acting and in consequence tend to reduce adsorption. Review of data given in Fig. 2 suggests that both factors may be operative.

A similar observation is noted when the clay is reacted initially with Ethomeen ions instead of aliphatic amines. In this case the natural clay surface is covered by polyoxethylene chains which may be regarded as superficially similar.

$$\diagup O\diagdown \quad | \quad \diagup O\diagdown \quad | \quad \diagup O\diagdown \quad | \quad \diagup O\diagdown$$
$$\qquad Si \qquad Si \qquad Si \qquad$$
$$\qquad | \qquad | \qquad | \qquad$$

$$\diagup O\diagdown \qquad\qquad \diagup O\diagdown \qquad\qquad \diagup O\diagdown$$
$$\qquad CH_2\,CH_2 \qquad CH_2\,CH_2$$

Again it is noted that maximum adsorption occurs when there is a definite balance between the hydrophilic and organophilic types of surface, and increase or decrease in the amount of either type of surface results in reduced adsorption.

In view of these findings it is suggested that adsorption occurs at both hydrophilic and organophilic surfaces; at the former by electrostatic/hydrogen bonding with the hydrophilic portion of the adsorbate molecule and at the latter by van der Waals bonding with the organophilic portion of the adsorbate molecule.
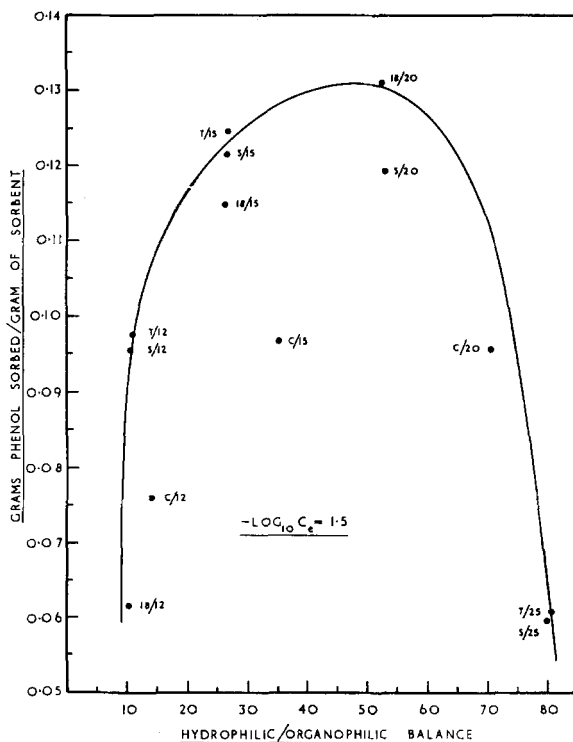

FIGURE 3.—The adsorption of phenol by Ethomeen clays as a function of hydrophilic/organophilic balance (H.L.B.).

The Nature of the Adsorbate Molecules

The data presented in Fig. 4 show how the positions of the substituting methyl and hydroxyl groups of the adsorbate molecule affect the magnitude of adsorption:

p-cresol $>$ m-cresol $>$ o-cresol, and
pyrocatechol $>$ resorcinol $>$ hydroquinone;
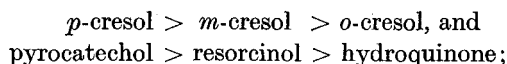
i.e. remoteness of the hydroxyl and methyl groups and proximity of two hydroxyl groups favor adsorption.
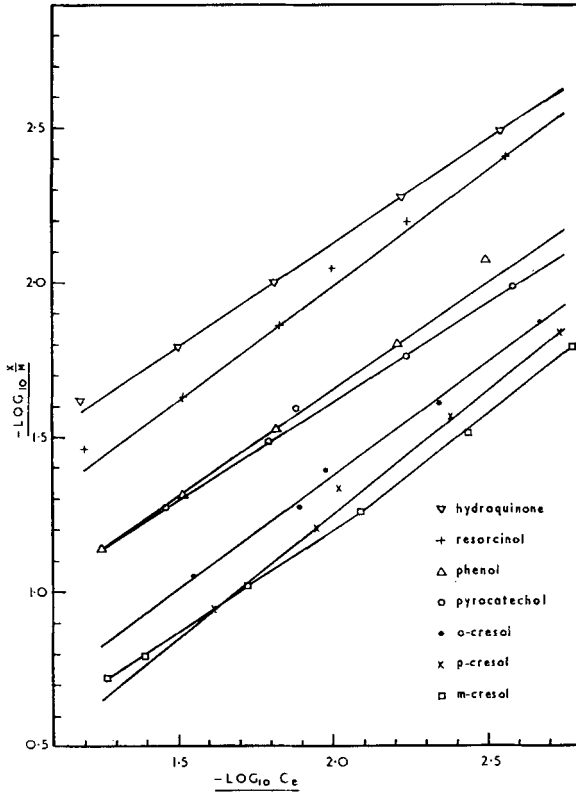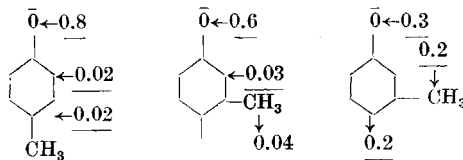

FIGURE 4.—Freundlich isotherms for the adsorption of monohydric and dihydric phenols by dodecylammonium bentonite.

Considering the electronic transitions which can occur in the cresols, by using a simple linear combination of atomic orbitals without the inclusion of overlap, the following values were obtained for the electron distribution.

It is noted that the highest discrete electron charge is observed when the two substituent groups are remote. Similarly it can be shown that in the dihydric phenol the reverse situation exists and proximity of the groups

is associated with a high discrete electron charge. Consideration of these electronic transitions in the light of adsorption data substantiates the original proposal for the adsorption mechanism and shows how for maximum adsorption the charge density of the adsorbate molecule must be localized.

Spatial Considerations

Since adsorbed phenol molecules occupy interlamellar positions in the organo–clay structure, consideration must be given to the adsorption data with respect to the available space.

In the series of *n*-alkyl ammonium bentonites, there is approximately 50 percent coverage of the clay surface with decylamine, but the interlamellar expansion is only 4 Å, which represents a monolayer of amine ions
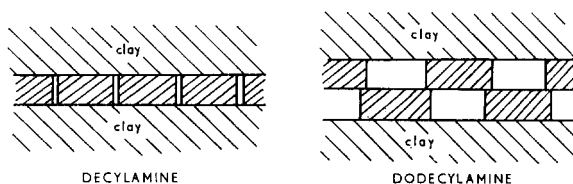

FIGURE 5.— Diagrammatic representation of the positioning of the amine ions in decylammonium and dodecylammonium bentonite.

between the lamellae (Jordan, 1949). The effective coverage is therefore nearer 100 percent and no further interlamellar adsorption can occur without expansion of the clay lattice. However, with dodecylamine, the lattice undergoes a further 4 Å expansion, consequently exposing 43.5 percent of natural clay surface (Fig. 5).

Since it is postulated that adsorption occurs at both hydrophilic and organophilic surfaces, it is reasonable to assume that maximum adsorption will occur when approximately equal amounts of each type of surface are available for the immediate condensation of adsorbate molecules. Decrease of amine size will result in the necessity for expansion of the lattice prior to adsorption, whilst increase of amine size will reduce the percentage of natural clay surface and hence reduce the strength of the electrostatic/hydrogen bonds. Both these effects will reduce the extent of phenol adsorption.

Thermodynamic Considerations

As with the majority of adsorption processes, the one under investigation is exothermic, and furthermore the partial molar heat of adsorption is a direct function of the amount of amine initially sorbed on the clay. Consideration of entropy changes involved show a general compatibility with the proposed theory of adsorption. At any one value of C_0, the entropy

change increases with increasing amount of amine present on the clay surface. The greater the amount of amine present, the less the space available for bifunctional adsorption of phenol molecules and hence the more ordered such molecules are when adsorbed—this is in fact observed (Table 3). By similar reasoning, it is noted that the more dilute the phenol starting concentration, the greater the entropy change involved when a standard amount is adsorbed onto a standard organo-clay surface.

TABLE 3.—THERMODYNAMIC QUANTITIES FOR ADSORPTION OF PHENOL
BY DODECYLAMMONIUM BENTONITE

Milliequi-valent of Amine on Clay	$-\Delta \bar{G}_m$ (cal mole^{-1})				$-\Delta \bar{H}_m$ (cal mole^{-1})				$-\Delta \bar{S}_m$ (cal mole^{-1} °C^{-1})			
	Value of C_0				Value of C_0				Value of C_0			
	0.1	0.05	0.02	0.01	0.1	0.05	0.02	0.01	0.1	0.05	0.02	0.01
70.0	79.4	94.2	101	129	850	1042	1300	1505	2.63	3.27	4.09	4.7
87.5	93.5	126	139	163	938	1183	1500	1745	2.88	3.61	4.65	5.4
104.5	107	145	171	188	1030	1335	1695	1965	3.15	4.06	5.22	6.07
121.0	126	159	214	251	1088	1413	1930	2175	3.28	4.28	5.85	6.57
138.0	141	179	214	232	1190	1543	2005	2335	3.28	4.65	6.11	7.18

Solubility of the Adsorbate in the Solvent

Since adsorption and solubility are different manifestations of the escaping tendency of the solute, adsorption should be greater if solubility is less. Referring to data given in Table 4, it is apparent that there is no correlation between $\Delta \bar{G}m$ and solubility and hence for this system, it must be assumed that the solubility effect is completely overridden by bonding and steric factors.

TABLE 4.—PARTIAL MOLAR FREE ENERGY VALUES FOR THE
ADSORPTION OF MONO AND DIHYDRIC PHENOLS BY DODECYL-
AMMONIUM BENTONITE

Phenol	$-\Delta \bar{G}_m$ (cal mole^{-1})	Solubility (g percent at 20 °C)
p-Cresol	298	2.2 (approx.)
m-Cresol	288	2.33
o-Cresol	219	2.2 (approx.)
Pyrocatechol	143	45.1
Phenol	123	8.3
Resorcinol	52	229.0
Hydroquinone	29	5.9

CONCLUSIONS

It has been shown that by exchanging the inorganic cations of montmorillonite for large amine ions, the material so produced possesses organophilic properties and as such exhibits preferential adsorption of soluble organic compounds from dilute aqueous solution. Several factors affect the extent of adsorption, but the main criteria appear to be the following: (1) The clay possesses areas of both hydrophilic and organophilic properties, the balance between the two types of surface being critical; and (2) the adsorbate molecule possesses a localized center of high electron density whilst the remainder of the molecule is essentially nonpolar.

It is proposed that adsorption occurs by two complimentary mechanisms — by electrostatic/hydrogen bonding between polar groups and by van der Waals bonding between organophilic centers. Substantiation of the theory is afforded by thermodynamic data, spatial considerations, and electron density measurements.

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